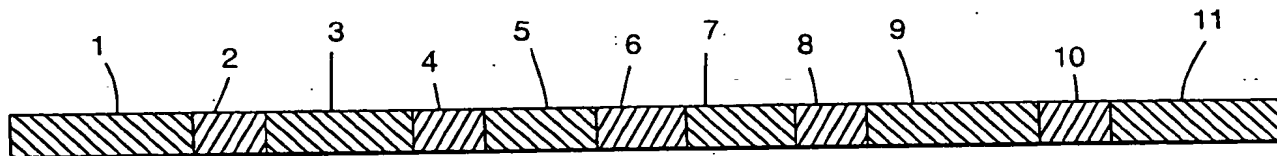


(54) Title: PROCESS FOR SOLVENTLESS COMPOUNDING AND COATING OF PRESSURE SENSITIVE ADHESIVE



A solvent-free hot melt process, for preparing a non-thermosettable, pressure-sensitive adhesive from a tackified non-thermoplastic hydrocarbon elastomer. The process employs a continuous compounding device that has a sequence of alternating conveying zones (1, 3, 5, 7, 9 and 11) and processing zones (2, 4, 6, 8 and 10). The processing zones masticate and mix materials in them. Non-thermoplastic elastomers having high molecular weight may be readily compounded into adhesives in the process.

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PROCESS FOR SOLVENTLESS COMPOUNDING AND COATING OF
PRESSURE SENSITIVE ADHESIVE

5 Field of the Invention

This invention relates to a solvent-free, hot melt process for the manufacture of a non-thermosettable, pressure sensitive adhesive (PSA) from a tackified, non-thermoplastic hydrocarbon elastomer.

10 Background of the Invention

Pressure sensitive adhesives based on non-thermoplastic hydrocarbon elastomers such as natural rubber, butyl rubber, synthetic polyisoprene, ethylene-propylene, polybutadiene, polyisobutylene, or styrene-butadiene random copolymer rubber, are well known in the art. The dominant means of
15 processing such adhesives comprises masticating the elastomer on a two roll mill or in a Banbury type internal mixer, dissolving the elastomer and other adhesive components in a hydrocarbon solvent, coating the solution onto a backing, and drying the coated product to remove the solvent. This technology is discussed in Handbook of Pressure Sensitive Adhesive Technology, D. Satas
20 (ed.), p. 268. Van Nostrand, N.Y., (1989). The solvent process has the disadvantages of being labor intensive, having low production rates, and emitting large amounts of potentially hazardous solvents to the atmosphere thereby requiring expensive equipment for solvent recovery and/or incineration. Moreover, such solvent based processes have become increasingly undesirable
25 for use in making adhesive tapes because of increasing environmental and safety regulations throughout the world.

A processing method, sometimes used when a relatively thick adhesive layer is desired, comprises masticating the elastomer as described above, blending the rubber and other adhesive components in an internal mixer such as
30 a Banbury mixer, and calendering the solid adhesive onto a backing using a three or four roll calender stack. The calendering process does not use solvent

but does require very expensive equipment. Additionally, this process is slow, and is only economical when adhesive coatings greater than about 2 mils (51 μm) thick are desired. An application of the calendering process is discussed in U.S. Patent No. 2,879,547 to Morris.

5 Environmental considerations, lower initial capital investments, potentially higher production rates, and lower processing costs have led to accelerated interest in the use of continuous hot melt compounding and extrusion coating of thermoplastic adhesive compositions. The elastomers employed in this technique are "thermoplastic" elastomers of the block
10 copolymer type, including for example, styrenic-diene block copolymers. Such materials exhibit a sharp reduction in viscosity at temperatures above 100°C where the styrene domains soften. Upon cooling, the domains reform and the material regains its rubbery character and cohesive strength. Illustrative teachings of adhesive formulations and processes of this type are found, for example,
15 in U.S. Patent No. 3,932,328 to Korpman, U.S. Patent 4,028,292 to Korpman, and U.S. Patent No. 4,136,071 to Korpman. The technology is further discussed in Handbook of Pressure Sensitive Adhesive Technology, pp. 317-373, D. Satas (ed.), Van Nostrand, N.Y., (1989).

Hot melt pressure sensitive adhesives based on these thermoplastic
20 elastomers have found wide acceptance in the packaging, label, and diaper closure markets, but limited acceptance for use in paper masking tapes. The adhesive properties of pressure sensitive adhesives made from these thermoplastic elastomers differ from those of adhesives based on non-thermoplastic hydrocarbon elastomers, and are undesirable for many tape
25 applications.

Because of their unique adhesive properties, non-thermoplastic hydrocarbon elastomer based adhesive systems, especially those employing natural rubber, are likely to be retained for many applications for which the thermoplastic elastomer systems are not adequate. Consequently, there is a
30 need to provide a method of making adhesives from these non-thermoplastic

elastomers which is environmentally appropriate, economically viable, and energy conserving.

Hot melt extrusion of pressure sensitive adhesives employing non-thermoplastic hydrocarbon elastomers such as natural rubber has been shown.

- 5 However, low molecular weight plasticizing aids such as processing oils, elastomer oligomers, waxes, or other materials defined and described as plasticizers in Dictionary of Rubber, K.F. Heinisch, pp. 359-361, John Wiley & Sons, New York, (1974), are used as major components in the adhesive formulations. These plasticizing aids ease processing but detract from the
- 10 ability of the finished adhesive to sustain a load and are generally known in the art to degrade adhesive performance.

- Canadian Patent No. 698,518 to P. Beiersdorf & Co., discloses a solventless extrusion coating process for coating a PSA composition based on non-thermoplastic elastomers including natural and synthetic rubber, high
- 15 molecular weight polyisobutylene and polyvinyl ether. The elastomer is pre-masticated and blended in a separate, batchwise operation using conventional rubber processing equipment such as a two-roll mill or a Banbury mixer. The preformed, compounded mixture is then fed to a heated single screw extruder and the molten coating is extruded onto a moving web. Plasticizing aids
- 20 comprising up to 54% of the formulation are used. It is believed that these plasticizing aids are used to accommodate the coating difficulties normally associated with the extrusion of high viscosity elastomers.

- Japanese patent application Shou 50-37692 to Fukugawa et al discloses a similar process of pre-masticating mixtures of ingredients of pressure sensitive
- 25 adhesives for 25 minutes, supplying the premasticated mixtures to a heated extruder, extruding the materials at 230°C onto a substrate, and curing the extruded materials by exposing them to electron beam radiation to enhance the cohesive strength of the adhesive and improve the bond to the backing. This work describes a narrow range of materials including the non-thermoplastic
- 30 elastomers natural rubber and styrene-butadiene rubber (SBR). In the two examples utilizing natural rubber, the natural rubber was blended with a

styrene-butadiene elastomer and a plasticizing aid. The plasticizing aid equalled about 87.5% of the total rubber charge, and no tackifier resins were used. The non-natural rubber example included 25.8% plasticizing aid.

German provisional patent publication

- 5 P-19 54 214.4 to Pyton AG discloses an extrusion process for the preparation of pressure sensitive adhesives which does not necessitate a separate pre-mastication step. A twin screw extruder is used to continuously compound and coat a formulation comprised of five different types of materials. Natural rubber and/or partially vulcanized rubber, latex, polybutene with a molecular
- 10 weight between 70,000 and 200,000, and polyisobutylene with a molecular weight between 100,000 and 250,000 comprise the "cohesive component". Four other classes of ingredients are required to accommodate this process. These other ingredients include low molecular weight (less than 15,000) polybutene and polyisobutylene or native bitumen, reactive and/or non-reactive
- 15 resins, antioxidants, and various metal oxide fillers. No specific compositions are taught, but the levels of plasticizing aids such as bitumen, or the low molecular weight polyisobutylene or polybutene range from 10-20%.

- U.S. Patent no. 2,199,099 to Cunningham discloses that air and oxygen enriched gases can be used to facilitate the oxidative breakdown of natural
- 20 rubber in an internal mixer to reduce the molecular weight of the rubber. A continuous hot melt extrusion process that employs the air-assisted oxidative breakdown of natural rubber followed by the addition of tackifiers and phenolic resin vulcanizing agent to form a thermosettable adhesive is known. In this process the molecular weight of the natural rubber is reduced to such a degree
- 25 that when the phenolic resin is added, the combination of the rubber and resin can be processed at a temperature below that at which vulcanization occurs.

- The hot melt extrusion of non-thermoplastic hydrocarbon elastomers has not proven to be a commercially practical method of making pressure sensitive adhesives having the properties needed for PSA tapes, such as masking,
- 30 packaging and medical tapes. Furthermore such process technology is not envisioned for sustaining the dominant position of natural rubber elastomer, the

single largest use of non-thermoplastic hydrocarbon elastomers for these PSA tapes. According to the Handbook of Pressure Sensitive Adhesive Technology, solvent and/or water coating of PSA adhesives are the only practical techniques for making such tapes, especially when the PSA's are based upon high molecular weight hydrocarbon elastomers. As discussed above, these techniques are not entirely satisfactory. Thus, it would be desirable to provide a practical method of compounding non-thermoplastic hydrocarbon elastomers at molecular weights and compositions of interest to the PSA industry.

10

Summary of the Invention

A process has been discovered which overcomes the disadvantages of the prior art and permits the processing of non-thermoplastic hydrocarbon elastomers, especially high molecular weight non-thermoplastic hydrocarbon elastomers, without the need to employ either organic solvents or low molecular weight plasticizing aids.

The present invention comprises a process for the solvent free compounding of non-thermosettable PSAs based upon a tackified non-thermoplastic hydrocarbon elastomer. The process employs a continuous compounding device and hot melt processing techniques. The adhesive composition can be compounded without separate batch pre-mastication of the elastomer and without the use of significant amounts of plasticizing aids to reduce the viscosity of the composition to render it processable. Additionally, the adhesive composition can be applied to a moving web directly from the compounding device so as to provide a continuous method for the manufacture of a PSA tape.

The process of the invention can accommodate even high molecular weight hydrocarbon elastomers, for example viscosity average molecular weight (\bar{M}_v) of 250,000 or more. As discussed above, it has been previously thought that such elastomers could only be compounded and applied if solvent or water

30

processing techniques were utilized or if significant amounts of low molecular weight plasticizing aids were employed.

The process can employ either aerobic or anaerobic processing. For purposes of this invention, aerobic processing means that gas which contains
5 available oxygen (such as compressed air) is intentionally injected into the compounding device so as to promote oxidative breakdown of the hydrocarbon elastomer. Anaerobic processing means that no oxygen-available gas is intentionally injected into the compounding device. However, minor amounts of air may be present in anaerobic processing in the practice of the invention.

10 Aerobic processing may be advantageously utilized when the hydrocarbon elastomer will preferentially undergo chain scission rather than crosslinking and/or chain extension. Aerobic processing allows a greater reduction in the molecular weight of the elastomer in a relatively short period of time. Additionally, aerobic processing allows manufacture at lower
15 temperatures. As a result, thermally sensitive materials may be compounded with the hydrocarbon elastomer in the process of the invention.

Anaerobic processing may be advantageously utilized when elastomers which crosslink under oxidative conditions are used. This mitigates the problem of these elastomers crosslinking during processing. Anaerobic processing may
20 also be used with elastomers that do not crosslink under oxidative conditions so as to achieve a higher molecular weight than would be achieved under aerobic conditions. This increases the cohesive strength of the adhesive and minimizes the degree of later crosslinking needed to provide enhanced cohesive strength. Anaerobic processing of either type of elastomer also results in adhesives
25 having lower odor and lighter color.

The practice of the invention employs a continuous compounding device that has a sequence of alternating conveying and processing zones. The elastomer is continuously conveyed from one zone to the other by the device. The processing zones are capable of masticating the elastomer. They are also
30 capable of mixing additives into the elastomer.

In the process, a non-thermoplastic elastomer is fed to a first conveying zone of the compounding device. This first zone transports the elastomer to a first processing zone where the elastomer is masticated. The masticated elastomer is then transported to a second conveying zone where a tackifier is
5 added and the mixture of the two is carried to a second processing zone where the tackifier and the masticated elastomer are mixed together to form a blend of the two materials. The blend can then be discharged from the compounding device and stored for later use. Alternatively, the blend can be applied to a web, preferably a moving web, in the form of a thin film.

10 In order to facilitate the description of the invention, the following terms used herein shall have the following meanings:

Non-thermosettable PSA shall mean a PSA which does not go to a relatively infusible and tack free state upon exposure to heat.

Non-thermoplastic hydrocarbon elastomer shall mean a hydrocarbon
15 homopolymer or copolymer as distinguished from a block copolymer.

Pressure sensitive adhesive shall mean an adhesive which is normally tacky at room temperature and adheres to a surface upon mere contact to the surface without the need for more than finger or hand pressure.

Tackifier shall mean a material which is miscible with at least one
20 hydrocarbon elastomer employed in the process, has a number average molecular weight \bar{M}_n of 10,000 grams per mol (g/mol) or less and a glass transition temperature (T_g) of -30°C or more as measured by differential scanning calorimetry (DSC).

Plasticizing aid shall mean a material which has a \bar{M}_n of less than
25 50,000 g/mol and a (T_g) of less than -30°C . as measured by DSC.

Brief Description of the Drawings

Figure 1 is a schematic representation of a continuous compounding and coating line useful in the practice of the invention.

30 Figure 2 is a schematic representation of an alternative continuous compounding and coating line useful in the practice of the invention.

Figure 3 is a schematic representation of the extruder screw design employing 9 zones.

Figure 4 is a schematic representation of the extruder screw design employing 11 zones.

5

Detailed Description of the Invention

The process of the invention employs a continuous compounding device. A number of such devices are known. They may comprise a single unit or a
10 series of units interconnected so as to continuously process the elastomer. The device has a sequence of alternating conveying and processing sections which are interconnected. An example of a continuous compounding device useful in the present invention is a twin screw extruder having a sequential series of conveying and processing zones. A plurality of input openings are provided
15 along the length of the extruder to facilitate the addition of various materials such as tackifier resins, fillers, antioxidants, plasticizing aids (if desired), radiation enhancers such as electron beam sensitizers and photoinitiators, and other adjuvants known in the art. Additions of material, whether elastomer, tackifier, or other adjuvants, are made through input ports to a partially full
20 conveying zone or zones. A melt pump and filter may be present either as an integral part of the extruder, or as a separate unit to facilitate both the removal of the adhesive from the compounding device and the removal of unwanted contaminants from the adhesive stream.

In the practice of the process, the elastomer is added to a first conveying
25 zone of the compounding device at a controlled rate so that the elastomer does not completely fill the zone. The elastomer may be pelletized by grinding or extrusion pelletization prior to being fed to the compounding device. Alternately, it may be fed directly into the compounding device without grinding or pelletization using a device such as a Moriyama extruder. If the
30 elastomer has been pelletized, it is preferably treated with a material such as talc to prevent agglomeration of the pellets.

The elastomer is then transported by the first conveying zone to a first processing zone where it is masticated. The first processing zone typically is designed to be essentially completely full and to masticate the elastomer.

Additionally, the processing zone conveys the elastomer to the next zone. It

- 5 may be desirable to provide the first processing zone as at least two discrete processing sections separated from each other by a transporting section. This permits the elastomer to be masticated in steps, with cooling of the masticated elastomer between each step.

If two or more elastomers are to be processed in the invention, they may

- 10 both be added to the first conveying zone and masticated in the first processing zone. Alternatively, the elastomers may be added sequentially to different conveying zones with sequential mastication after each elastomer addition. Sequential elastomer addition to different conveying zones may also be employed when a single elastomer is used.

- 15 If aerobic processing is desired, a gas containing available oxygen, such as compressed air, can be readily injected into the compounding device. Preferably air is injected into either a transporting section, or a conveying zone situated between two processing zones. Alternatively, the gas can be injected into any processing or conveying zone. If the gas comprises compressed air, it
- 20 is typically injected into the compounding device at a pressure of from 5 to 100 pounds per square inch gauge (psig) (30-700 kilopascals (kPa)). Table I illustrates the relationship between air pressure and inherent viscosity for a smoked sheet natural rubber.

TABLE I

	<u>Compressed Air Pressure</u>			<u>Flow Rate</u>	<u>IV</u>
	(psig)	(kPa)		SCFM (4h)	
5	60	414	35	992	1.59
	45	310	35	992	1.64
	30	207	35	992	1.73
	20	138	35	992	1.78
	10	69	35	992	1.81
10	0	0	35	992	1.82

The natural rubber was masticated in the extruder used in Example 19. The screw speed was 180 rpm. The melt temperature was maintained at 163°C throughout the extruder. Air was injected and bled from zone 3 of the extruder. The rubber was fed to the extrudate at a rate of 57.8 kg/hr. A flow meter may be used to regulate the air flow to the compounding device. Additionally, a pressure control valve may be used to build or release air pressure in the extruder.

Mastication is preferably carried out in the absence of materials which will lubricate the elastomer and prevent reduction of its molecular weight. This does not however, preclude the presence of small amounts of such materials, provided that the amount present does not effectively reduce the rate of mastication. Certain other solid adjuvants, such as talc, inorganic fillers, antioxidants, and the like, may be fed to the compounding device such that they are present during mastication.

The masticated elastomer then passes from the first processing zone to a second conveying zone. As with the first conveying zone, the second conveying zone is not completely filled by the elastomer. Tackifier, and optionally other additives, are fed to the second conveying zone. The resulting mixture is conveyed to the next processing zone where they are mixed to form a blend of the materials. A number of techniques may be used to feed these materials to the compounding device. For example, a constant rate feeder such as a K-Tron loss-in-weight feeder may be used to add solid materials. Heated

pail unloaders, gear pumps, and other appropriate equipment for feeding liquids at a controlled rate may be used to feed the liquids to the compounding device. Additives present at low concentration may be pre-blended with one or more of the other components for more accurate addition.

5 Although substantially all mastication occurs in the first processing zone, there may be some mastication which occurs in subsequent processing of the elastomer through the compounding device. This additional mastication may occur in subsequent conveying or processing zones. In any event, the degree to which the elastomer must be masticated in the practice of
10 the invention varies with each elastomer employed and the finished product desired. Generally, the elastomer must be sufficiently masticated to (i) permit subsequently added tackifiers and any other adjuvants to be satisfactorily mixed into the elastomer to form a blend and (ii) to permit the blend to be extruded as a stream that is essentially free from both rubber particles and from visually
15 identifiable regions of unmixed tackifier and any other adjuvants.

 Once the masticated elastomer, tackifier, and any other adjuvants have been formed into the blend, the composition may now be referred to as an adhesive. This adhesive typically has a viscosity at the processing temperature in the range from 500 Poise to 5000 Poise (measured at a shear rate of 1000
20 sec⁻¹). Higher viscosity adhesives may also be processed in the process of the invention. The processing temperature of the adhesive is typically in the range of 100-200°C.

 The adhesive may be discharged from the compounding device into a storage container for later additional processing or use. Alternatively, it
25 may be discharged directly onto a support in the form of a thin film. Preferably, the support comprises a moving web. The thin adhesive film may be formed by pumping the adhesive through a coating die, optionally with the aid of a gear pump or other suitable device to develop sufficient pressure. The die is preferably of the contacting variety (i.e. not a drop die) which smears the
30 adhesive onto a moving web supported on a backup roll. The die may have a flexible blade, a cylindrical rubber wipe, or a rotating cylindrical metal rod on

the downstream side of the die opening to spread the adhesive. The die may be located at the output of the compounding device to allow coating in-line with the compounding and extruding operations. Alternatively, the adhesive may be discharged from the compounding device and fed to the coating die using a
5 separate extruder, melt pump, or combination of extruder and melt pump with sufficient pressure to force the adhesive mixture through the die. The adhesive may optionally be filtered prior to feeding to the coating die.

The coated adhesive may optionally be crosslinked by exposure to ionizing radiation, such as electron beam or ultraviolet radiation, to enhance
10 the cohesive strength of the material. Crosslinking may be carried out in-line with the coating operation or may occur as a separate process. The degree of crosslinking achieved is a matter of choice and is dependent upon a number of factors such as the end product desired, the elastomer used, the thickness of the adhesive layer, etc. Techniques for achieving crosslinking via exposure to
15 activating radiation are known to those of skill in the art.

A release coating may also be optionally applied to the web, either before or after application of the adhesive. The release coating may be continuous or discontinuous on the web and is normally on the surface of the web opposite that which ultimately bears the adhesive. The release coating may
20 be applied either in-line with the coating or crosslinking operations, or as a separate process.

A twin screw extruder is preferably used as the compounding device in the invention. The extruder screw should be configured to masticate the elastomer in the first processing zone prior to addition of the tackifier.
25 Additionally, if a blend of elastomers is used in the adhesive, the first processing zone preferably allows mastication and blending of the elastomer components. The portion of the extruder and screw following the first processing zone must be designed to permit the addition of the tackifier and other additives to the elastomer and good mixing of the elastomer with these
30 materials. Preferably, the screw is designed so that a homogeneous adhesive composition results.

The design of the screw to achieve mastication, conveying and blending follows normal practices known in the art. Namely, the screw has a sequence of conveying and processing zones. Flow restriction and mixing elements are provided so as to achieve appropriate flow along the screw and
5 obtain appropriate mastication and mixing. The conveying zones may contain ordinary Archimedes screw elements. The processing zones may contain kneading blocks, pin mixers, or other elements designed for mastication, compounding and mixing. Flow restriction elements, such as kneading blocks arranged with a reverse pitch, reverse pitched conveying screws, a disk element
10 or other device designed to restrict the flow of material, may also be present in the processing zone to ensure that the portion of the processing zone preceding these elements tends to run full of material while the conveying zone following them tends to run only partially full.

A wide variety of non-thermoplastic hydrocarbon elastomers can
15 be employed in the present invention. These materials may be used singly or blended together in the practice of the invention. Examples of these elastomers include, natural rubber, butyl rubber, synthetic polyisoprene, ethylene-propylene rubber, ethylene-propylene-diene monomer rubber (EPDM), polybutadiene, polyisobutylene, poly(alpha-olefin) and styrene-butadiene
20 random copolymer rubber. These elastomers are distinguished from thermoplastic elastomers of the block copolymer type such as styrenic-diene block copolymers which have glassy end blocks joined to an intermediate rubbery block.

Tackifiers useful in the invention preferably have a low
25 molecular weight relative to the hydrocarbon elastomer, and a Tg higher than that of the hydrocarbon elastomer.

Examples of useful tackifiers include rosin and rosin derivatives, hydrocarbon tackifier resins, aromatic hydrocarbon resins, aliphatic hydrocarbon resins, terpene resins, etc. Typically the tackifier comprises from
30 10 to 200 parts by weight per 100 parts by weight of the elastomer.

A number of adjuvants may also be used in the adhesive. Examples of such adjuvants include antioxidants, such as hindered phenols, amines, and sulphur and phosphorous hydroperoxide decomposers; inorganic fillers such as talc, zinc oxide, titanium dioxide, aluminum oxide, and silica; 5 plasticizing aids such as those materials described as plasticizers in the Dictionary of Rubber, K. F. Heinisch, pp. 359, John Wiley & Sons, New York (1974), oils, elastomer oligomers and waxes; and the like. Typically the antioxidant comprises up to 5 parts by weight per 100 parts by weight elastomer; the inorganic filler comprises up to 50 parts by weight per 100 parts 10 by weight of elastomer; and the plasticizing aids up to 10 percent by weight of the total adhesive. Preferably, the use of plasticizing aids is unnecessary.

A number of organic and inorganic materials may be used as the web in the practice of the present invention. Such materials include polymeric films, metallic foils, paper, ceramic films, and the like. Furthermore, the web 15 may comprise a plurality of fibers in a mat-like construction. The fibers may be combined to form either a woven or a non-woven (i.e., randomly arranged collection of fibers) web.

Virtually any PSA tape can be made by the process of the invention. Examples of such tapes include masking tape, packaging tape (such 20 as box sealing and strapping tapes), decorative tape, protective tape and film, label stock, diaper closure tape, medical tape (such as hospital and athletic tapes), etc. Additionally, the process can be used to make any article having a layer of a hydrocarbon elastomer-based PSA on a backing.

This invention is illustrated by the following examples, but the 25 particular materials and amounts thereof recited in these examples, as well as other conditions and details should not be construed to unduly limit this invention.

A schematic representation of a continuous compounding, coating and crosslinking equipment configuration of the type used in the invention is 30 shown in Figures 1 and 2. The configuration represented by Figure 1 was used in Examples 1-13. The configuration represented by Figure 2 was used in

Examples 14-19. Various screw configurations were used throughout the examples. Figure 3 is a schematic representation of the screw used in Examples 1-18. Figure 4 is a schematic representation of the screw used in Example 19.

5 The compounding device employed in both Figures 1 and 2 was a Werner-Pfleiderer co-rotating twin screw extruder 20. A model ZSK-30 extruder was used in Examples 1-16. A model ZSK-90 extruder was used in Examples 17-19.

 The extruders 20 and 21 were equipped with an elastomer feed
10 hopper 22 and solids feed hoppers 24 and 26. Feed hoppers 22, 24 and 26 controlled the rate of material delivered to the extruders 20 and 21 by continuously monitoring the weight of material in the feed hopper. A vent 27 was provided near the discharge end of each of the extruders 20 and 21.

 With reference to Figure 1, a Zenith gear pump 28 was provided
15 to meter the adhesive melt through filter 30 and die 32. Excess adhesive was dumped through a dump valve (not shown) by the pressure generated in extruder 20. Coating die 32 deposited a desired thickness of adhesive onto web 34 which passed around a coating roll 36. The die 32 was a 6 inch (15.2 cm) wide die with a rubber wipe on the downstream side of the orifice. The coating
20 roll 36 was a chromed steel roll which was temperature controlled by circulating heated water through its interior. An electron beam crosslinking station 38 was also provided.

 An alternative equipment configuration useful in the practice of the invention is schematically shown in Figure 2. In this configuration, a single
25 screw extruder 23 is interposed between the twin screw extruder 21 and the filter 30. The single screw extruder 23 is used to generate enough pressure to push the adhesive through the filter 30. Additionally, the Zenith gear pump 28 was used downstream of the filter to meter the adhesive to die 33. The die 33 was a 24 inch (61 cm) wide contact extrusion die with a rotating steel rod on
30 the downstream side of the die to smear the adhesive onto the web. The coating roll 37 was a temperature controlled steel roll having a rubber coating

on it. The line speed of this configuration was automatically adjusted to achieve the desired coating thickness.

The screw designs employed in the Examples are shown schematically in Figures 3-4. The screw design of Figure 3 contained 9 zones.

- 5 The screw design of Figure 4 contained 11 zones. Zones 1, 3, 5, 7, 9 and 11 (if present) comprised conveying zones. Zones 2, 4, 6, 8 and 10 (if present) comprised processing zones. The dimensions of the various zones of each screw design are set out in Table II, as are the Examples in which each design were used.

10

TABLE II

Screw Design	Fig.3	Fig. 3	Fig. 3	Fig.4
Used in Ex's.	1-13	14-16	17-18	19
Diameter (mm)	30	30	90	90
15 Length (mm)	1160	1172	3380	3382
Zone 1 (mm)	186	168	1000	482
Zone 2 (mm)	70	84	260	240
Zone 3 (mm)	154	125	440	230
Zone 4 (mm)	56	84	200	240
20 Zone 5 (mm)	112	122	420	260
Zone 6 (mm)	84	42	320	40
Zone 7 (mm)	94	126	100	180
Zone 8 (mm)	84	70	160	240
Zone 9 (mm)	320	351	400	360
25 Zone 10 (mm)	-	-	-	240
Zone 11 (mm)	-	-	-	870

Example 1

- Natsyn™ 2210 synthetic polyisoprene (available from Goodyear
 30 Tire and Rubber Co.) was pelletized using a Moriyama pelletizer and dusted with talc. This material was then fed to Zone 1 of the twin screw extruder 20

at a rate of 68.0 g/min using a K-Tron loss-in-weight feeder which continuously monitored the weight of the material in the hopper. The elastomer and talc were transported from Zone 1 to Zone 2 by the screw and was masticated in Zone 2. The elastomer was transported through zones 3 and 4 where additional
5 mastication occurred, to zone 5 where a sample of the elastomer was removed and found to have an inherent viscosity (IV) of 2.68 dl/g in toluene measured at a concentration of 0.15 grams per deciliter (g/dl).

Arkon™ P-115 hydrogenated tackifier resin (available from Arakawa Chemical Industries, Ltd.) was dry blended with Irganox™ 1010
10 antioxidant (available from Ciba-Geigy Corp.) at a ratio of 49 parts by weight of resin to 1 part of antioxidant. This blend was fed to the extruder 20 in Zone 5 through feed hopper 24 at a rate of 36.7 g/min. A K-Tron loss-in-weight feeder was used to monitor the weight in hopper 24. A total of 53 parts by weight of tackifier per 100 parts by weight of elastomer was fed to the extruder
15 20. The adhesive was transported through the remaining zones of the extruder and delivered to metering pump 28. The metering pump 28 (See Fig. 1) was set to deliver 46.2 g/min of adhesive to the extrusion die 32 which coated the adhesive 4.75 inches wide (12 cm) on a creped paper masking tape backing moving at 30 ft/min (9.1 m/min) for an average coating thickness of 1.65 mils
20 (41 μ m). The melt temperature throughout the extruder was maintained at approximately 150°C. The coating roll 36 was maintained at a temperature of 90°C. The screw speed was maintained at 400 rpm. The resulting coated web comprised a PSA masking tape.

25

Example 2

Example 1 was repeated except that after being coated onto the creped paper backing, the backing continued to move at 30 ft/min (9.1 m/min) and the adhesive layer was exposed in line to electron beam radiation at a dose of 6 MRads. The irradiated PSA masking tape had improved cohesive strength.

30

Example 3

The equipment and conditions employed in Examples 1 were repeated in Example 3 with the following exceptions. Smoked sheet natural rubber (available from The Ore and Chemical Company, Inc.) was ground to particles approximately one quarter inch (0.63 cm) in diameter and dusted with talc. The rubber particles were fed to Zone 1 of the twin screw extruder 20 at a rate of 68.0 g/min. The elastomer and talc were transported from Zone 1 to Zone 2. The elastomer was masticated there and was then transported through zones 3 and 4, where additional mastication occurred, to zone 5 where a sample of the elastomer was removed and found to have an inherent viscosity of 4.7 dl/g in toluene measured at a concentration of 0.15 g/dl.

Piccolyte™ A-135 alpha-pinene tackifying resin (available from Hercules Chemical Company, Inc.) was dry blended with Irganox™ 1010 antioxidant at a mass ratio of 55:1 tackifier to antioxidant. A total of 55 parts by weight of tackifier per 100 parts by weight of elastomer was fed to the extruder 20. The blend of tackifier and antioxidant was fed to Zone 5 of the extruder at a rate of 38.1 g/min. The compounded adhesive was passed through the remaining zones of the extruder and was metered to the extrusion die at a rate of 46.2 g/min to coat 4.75 inches wide (12 cm) on a creped paper backing moving at 30 ft/min (9.1 m/min). The melt temperature of the adhesive was maintained at approximately 165°C throughout the extruder. The resulting adhesive tape was useful as a masking tape.

Example 4

Example 3 was repeated except the adhesive was extruded at a rate of 46.2 g/min to coat 4.75 inches wide (12 cm) onto a 1.5 mil (37 μm) thick poly(ethylene terephthalate) backing moving at 30 ft/min (9.1 m/min). The resulting coated web continued to move at a speed of 30 ft/min (9.1 m/min) and the adhesive layer was then exposed to electron beam radiation at a dose of 5 MRads. Both the unirradiated and the irradiated PSA tapes were useful as a protective tape. The irradiated tape had improved cohesive strength.

Example 5

Example 3 was repeated except that, after being coated, the PSA tape continued to move at a speed of 30 ft/min (9.1 m/min) and the adhesive layer was exposed in line to electron beam radiation at a dose of 3 MRads.

5 The resulting irradiated tape had improved cohesive strength.

Example 6

Example 1 was repeated with the following changes. Pelletized Natsyn™ 2210 and ground smoked sheet natural rubber were fed to Zone 1 of the twin screw compounder 20 using separate feed hoppers. The Natsyn™ 2210 was delivered at a rate of 34.2 g/min. The natural rubber was added at a rate of 34.0 g/min. The elastomers and talcs were transported from Zone 1 to Zone 2 where the elastomers were masticated.

Piccolyte™ A-135 tackifier was pre-blended with Irganox™ 1010 antioxidant at a mass ratio of 55:1 tackifier to antioxidant and the blend was fed to Zone 5 of the extruder at a rate of 38.1 g/min. A total of 55 parts by weight of tackifier per 100 parts by weight of elastomer was fed to the extruder 20. The adhesive was transported through the remaining zones of the extruder and was delivered to the extrusion die at a rate of 46.2 g/min. It was coated onto a 1.5 mil (38 μm) polyester film at a width of 4.75 inches (12 cm) using a line speed of 30 ft/min (9.1 m/min) to form an adhesive coating 1.6 mils (40 μm thick). The melt temperature was maintained at approximately 165°C throughout the extruder. The resulting PSA tape was useful as a protective tape.

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Example 7

Example 6 was repeated except that, after being coated, the PSA tape continued to move at a rate of 30 ft/min (9.1 m/min) and the adhesive layer was exposed in line to electron beam radiation at a dose of 6 MRads.

30 The resulting PSA tape had improved cohesive strength.

Example 8

Example 1 was repeated with the following changes. A controlled Mooney viscosity natural rubber (SMR CV60) (available from The Ore and Chemical Company, Inc.) was pelletized using the Moriyama pelletizer and the pellets dusted with talc. Similarly, Budene™ 1207 cis-polybutadiene (available from Goodyear Tire & Rubber Company) was pelletized and talc coated. The two elastomers were fed to Zone 1 of the twin screw compounder using separate feed hoppers. The CV60 natural rubber was delivered at a rate of 31.9 g/min. The Budene™ 1207 was fed at 36.5 g/min. The elastomers and talcs were transported from Zone 1 to Zone 2 where the elastomers were masticated.

Pentalyn™ H rosin ester tackifier (available from Hercules Chemical Company, Inc.) was dry blended with Irganox™ 1010 antioxidant at a mass ratio of 65.7:1 tackifier to antioxidant. The blend was fed to Zone 5 of the twin screw compounder at a rate of 45.6 g/min. A total of 66 parts by weight tackifier per 100 parts by weight of elastomer was fed to the extruder. The adhesive was transported through the remaining zones of the extruder and metered to the extrusion die at a rate of 46.1 g/min. The adhesive was coated on a creped paper masking tape backing at a coating thickness of 1.6 mils (40 μm). The web was running at 30 ft/min (9.1 m/min) and was coated 4.75 inches (12 cm) wide. The melt temperature was maintained at approximately 150°C throughout the extruder. The resulting adhesive tape was useful as a PSA masking tape.

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Example 9

Example 8 was repeated except that, after being coated, the PSA tape continued to move at a rate of 30 ft/min (9.1 m/min) and the adhesive layer was exposed in line to electron beam radiation at a dose of 4 MRads. The irradiated PSA tape had improved cohesive strength.

Example 10

Example 1 was repeated with the following changes. Smoked sheet natural rubber ground as described in Example 3 was used as well as Ameripol/Synpol 1011A styrene-butadiene random copolymer rubber (SBR) (available from Ameripol/Synpol Company). The SBR was pelletized and talc coated using the Moriyama system. The two rubbers were both fed to Zone 1 of the twin screw compounder using separate feed hoppers. The natural rubber was fed at a rate of 34.0 g/min. The SBR was fed at 34.2 g/min. The elastomers and talcs were transported from Zone 1 to Zone 2 where the elastomers were masticated.

Escorez™ 1304 petroleum derived tackifying resin (available from Exxon Research & Engineering Co.) was dry blended with Irganox™ 1010 antioxidant at a mass ratio of 50:1 tackifier to antioxidant. The blend was fed to Zone 5 of the twin screw compounder at a rate of 34.9 g/min. A total of 50 parts by weight of tackifier per 100 parts by weight of elastomer was fed to the extruder 20. The adhesive was transported through the remainder of the extruder and was metered to the extrusion die at a rate of 46.1 g/min. The adhesive was coated onto a creped paper masking tape backing to 4.75 inches wide (12 cm) at 30 ft/min (9.1 m/min) resulting in an average adhesive thickness of 1.6 mils (40 μm). The melt temperature was maintained at approximately 140°C throughout the extruder. The resulting adhesive tape was useful as a PSA masking tape.

Example 11

Example 10 was repeated except that, after being coated, the PSA tape continued to move at a rate of 30 ft/min (9.1 m/min) and the adhesive layer was exposed in line to electron beam radiation at a dose of 6 MRads. The irradiated PSA tape has improved cohesive strength.

Example 12

Example 1 was repeated with the following exceptions.

Controlled Mooney viscosity natural rubber (CV60) was pelletized using the Moriyama pelletizer and dusted with talc. The elastomer was added to Zone 1 of the extruder at a rate of 68.4 g/min. The elastomer and talc were transported from Zone 1 to Zone 2 and were masticated in Zone 2. The elastomer and talc were transported through zones 3 and 4, where additional mastication occurred, to zone 5 where a sample of the elastomer was removed and found to have an IV of 3.5 dl/g in toluene when measured at a concentration of 0.15 g/dl.

Escorez™ 1304 tackifier resin was dry blended with Irganox™ 1010 antioxidant and zinc oxide in the following amounts:

	<u>Component</u>	<u>Wt. %</u>
15	Escorez™ 1304	78.2
	Zinc Oxide 20.8	
	Irganox™ 1010	1.0

This blend was added to Zone 5 of the twin screw compounder at a rate of 70.6 g/min. A total of 81 parts by weight of tackifier per 100 parts by weight of elastomer was fed to the extruder. White mineral oil was added to the extruder in Zone 7 through an injection port (not shown). A Zenith gear pump delivered the oil to the extruder from an open stainless steel container. The oil was delivered by a gear pump at a rate of 8.34 g/min. A total of 12 parts by weight of oil per 100 parts by weight of elastomer were fed to the extruder. The resulting adhesive contained 5.6% oil by weight. The adhesive passed through the remaining zones of the extruder and was metered to the extrusion die at a rate of 104 g/min. It was coated 4.75 inches wide (12 cm) onto a cotton cloth backing moving at 30 ft/min (9.1 m/min) to form an adhesive coating averaging 3.6 mils (91 μ m) thick. The melt temperature was maintained at approximately 165°C throughout the extruder. The resulting adhesive tape was useful as a medical tape. The tape, including the adhesive

layer, was porous. Such porosity allows perspiration and skin oil to pass through the tape.

Example 13

5 Example 12 was repeated except that, after being coated, the PSA tape continued to move at a rate of 30 ft/min and the adhesive layer was exposed in line to electron beam radiation at a dose of 2 MRads using an accelerating potential of 175 kV. The irradiated PSA tape had improved cohesive strength. The adhesive layer retained its porosity.

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Example 14

Ribbed smoked sheet natural rubber was ground to particles approximately one quarter inch (0.63 cm) in diameter and dusted with talc. This was fed to Zone 1 of the twin screw extruder at a rate of 68.0 g/min. The
15 temperature in zones 2 through 4 was maintained at 168°C. After zone 5 the melt temperature was maintained at 110°C. Air was injected into and vented from zone 3 of the extruder. The pressure and flow rate were adjusted to achieve an IV of the rubber (as measured on samples removed at Zone 5) of 2.1 dl/g in toluene when measured at a concentration of 0.15 g/dl. The
20 extruder speed was 320 rpm. Escorez™ 1310 tackifier was blended with Bismaleimide M-20 available from Mitsui Petrochemical at a ratio of 65 parts of Escorez™ 1310 to 1 part of M-20 by weight. This mixture was then added to zone 5 at a rate of 44.9 g/min. A total of 65 parts by weight of tackifier per 100 parts of elastomer were added. Titanium dioxide was added to zone 7 at a
25 rate of 6.1 g/min. Liquid tricresyl phosphate was added to zone 9 at a rate of 2.0 g/min and liquid triphenyl phosphite was added to the same zone at a rate of 0.3 g/min. This resulted in a total liquid content of 2% of the adhesive. The compounded adhesive was coated on a creped paper masking tape backing using a die with a flexible steel blade. The web speed was 60 ft/min (18.2
30 m/min) and adhesive was coated at a thickness of 1.5 mils (38 μm). The adhesive layer of the moving web was irradiated by exposure to an electron

beam operating at an accelerating potential of 165 Kv with a dose of 2 MRads. The resulting irradiated PSA tape was useful as a masking tape.

Example 15

5 Controlled viscosity natural rubber (SMR CV 60) was pelletized with the Moriyama pelletizer and fed to zone 1 of the extruder at a rate of 68.0 g/min. The extruder speed was set at 470 rpm. The air pressure and flow rate in zone 3 was regulated to achieve an IV of the rubber (as measured on a sample removed at zone 5) of 1.5 dl/g when measured at a concentration of
10 0.15 g/dl. The temperature in zones 2 through 4 was maintained at 195°C. After zone 5 the melt temperature was maintained at 100°C. Wingtack Plus tackifying resin from Goodyear was blended with Irganox™ 1010 antioxidant from Ciba-Geigy at a ratio of 40.1 parts Wingtack Plus to 1.3 parts Irganox™ 1010 by weight. This blend was added to zone 5 at a rate of 50.5 g/min. A
15 total of 72 parts by weight of tackifier per 100 parts of elastomer were added. The compounded adhesive was coated onto a 2 mil (51 μm) biaxially oriented polypropylene film at a coating thickness of 1.5 mils (38 μm). The web was run at a speed of 30 ft/min. (9.1 m/min). The resulting product was useful as a PSA packaging tape.

20

Example 16

Example 15 was repeated except that, after being coated, the tape continued to move at a rate of 30 ft/min (9.1 m/min) and the adhesive layer was irradiated in line by exposure to an electron beam at a dose of 9 MRads.
25 The resulting PSA tape had increased cohesive strength.

Example 17

CV60 natural rubber was ground and dusted with talc. The rubber was added to Zone 1 of the extruder at a rate of 116 lb/hr. (52.7 kg/hr).
30 The extruder screw operated at 225 rpm. The elastomer and talc were transported from Zone 1 to Zone 2 and were masticated in Zone 2. Escorez™

1304 tackifier was added at a rate of 34.8 lb./hr (15.8 kg/hr) to zone 3. Additional Escorez™ 1034 was added at a rate of 59.2 lb/hr (26.9 kg/hr) to zone 5. Irganox™ 1010 was added with the tackifier stream to zone 5 at a rate of 1.2 lb/hr. (0.55 kg/hr). Zinc oxide was also fed to Zone 5 at a rate of 24.9 lb/hr (11.3 kg/hr). A total of 81 parts by weight of tackifier and 21 parts by weight of zinc oxide per 100 parts by weight of elastomer were fed to the extruder. White mineral oil was added to Zone 7 at 13.9 lb/hr (6.3 kg/hr). The resulting adhesive contained 5.6% oil by weight. The adhesive was metered to a 24 inch (61 cm) wide contact extrusion die with a rotating steel rod on the downstream side of the die gap to smear the adhesive onto the web. The adhesive was applied at a rate of 250 lb/hr (113.6 kg/hr) and coated onto a cotton cloth backing 24 inches (61 cm) wide. The line speed was automatically adjusted to achieve an adhesive coating thickness of 3.7 mils (94 μ m). The melt temperature was maintained at approximately 130°C throughout the extruder. The resulting PSA tape was useful as a porous medical tape.

Example 18

Example 17 was repeated except that, after being coated, the PSA tape continued to move at a rate that was automatically adjusted to maintain the adhesive coating thickness at 3.7 mils (94 μ m). The moving adhesive layer was exposed in line to electron beam radiation at a dose of 5 MRads. The irradiated PSA tape retained its porosity and had improved cohesive strength.

Example 19

Ground ribbed smoked sheet natural rubber was added to zone 1 of the twin screw compounder at a rate of 79.35 lb/hr. (36 kg/hr). Air was injected into and bled from zone 3. The air pressure and flow rate were regulated to achieve an IV of the rubber (as measured on a sample removed at zone 7) of 2.0 dl/g. in toluene when measured at a concentration of 0.15 g/dl.

The screw speed was 150 rpm and the extruder wall temperature in zones 2 through 5 was maintained at 200°F. (93)°C.

Escorez™ 1304 tackifying resin was added to zone 9 at a rate of 68.2 lb/hr (31 kg/hr). Titanium dioxide was added to zone 9 at a rate of 1.6 lb/hr (0.7 kg/hr). Irganox™ 1010 antioxidant was added to zone 9 at a rate of 0.8 lb/hr (0.36 kg/hr). The extruder wall temperatures in zones 7 through 11 were maintained at 250°F (121°C). The pumping extruder and transport lines were also maintained at 250°F (121°C). The adhesive was metered to the die at a rate of 150 lb/hr (68.1 kg/hr) and coated onto a creped paper masking tape backing. The line speed was adjusted automatically to achieve a coating thickness of 2 mils (51 μm). The adhesive layer of the moving web was irradiated in line by exposure to an electron beam radiation at a dose of 4 MRads. The PSA tape was useful as a masking tape.

Although the present invention has been described with respect to specific embodiments, the invention is not intended to be limited to those embodiments. Rather, the invention is defined by the claims and equivalents thereof.

Claims

1. A solventless hot melt process for preparing a non-thermosettable pressure sensitive adhesive from a tackified non-thermoplastic hydrocarbon elastomer in a continuous compounding device which has a sequence of alternating conveying and processing zones, said processing zones being capable of masticating and mixing, said process comprising the steps of:
- (a) feeding said hydrocarbon elastomer to a first conveying zone to transport the elastomer to a first processing zone;
 - 10 (b) masticating the elastomer in the first processing zone for a time sufficient to render it capable of (i) receiving adjuvants, and (ii) being extruded;
 - (c) transporting the masticated elastomer from the first processing zone to a second conveying zone, feeding tackifier to the masticated elastomer in the second conveying zone and transporting the combination of the masticated elastomer and tackifier to a second processing zone;
 - 15 (d) forming a blend of the masticated elastomer and tackifier in the second processing zone; and
 - 20 (e) discharging said blend from said continuous compounding device;
- wherein said blend comprises a pressure sensitive adhesive which contains less than 10 percent by weight of plasticizing aid.
2. A process according to claim 1 wherein the first processing zone comprises at least two sections separated from each other by a transporting section.
3. A process according to claim 2 wherein a gas containing available oxygen is injected into said transporting section.

4. A process according to claim 1 wherein said blend is discharged onto a moving web as a thin film thereon.

5. A process according to claim 4 comprising the further step of crosslinking said adhesive in line by exposure to ionizing radiation.

6. A process according to claim 1 comprising the further step of applying a release material to the surface of said web opposite the surface ultimately bearing said adhesive film.

10

7. A process according to claim 1 performed in the presence of less than 10% by weight of a plasticizing aid in a continuous twin screw compounding device operated at a desired speed wherein:

- 15 a) the elastomer is fed to the first conveying zone of the device at a controlled rate so that the elastomer does not completely fill the first conveying zone; and transporting the elastomer to the first processing zone of the device so that said elastomer essentially completely fills the first processing zone; and
- 20 b) masticating the elastomer in the first processing zone for a time sufficient to receive a subsequently added tackifier and form a blend thereof; and
- 25 c) transporting the masticated elastomer to a second conveying zone so that it does not completely fill the second conveying zone and feeding the tackifier to the second conveying zone at a controlled rate to form a mixture of masticated elastomer and tackifier; and
- d) transporting said mixture to a second processing zone so as to essentially fill the second processing zone with the mixture and

forming a blend of the mixture in the second processing zone;
and

e) discharging said blend from said device.

5 8. A process according to claim 7 wherein said blend is
discharged from said device onto a moving web to form a layer of a pressure
sensitive adhesive on said moving web.

9. The process of claim 8 wherein the adhesive layer on said
10 moving web is exposed to ionizing radiation.

10. A process according to claim 1 which employs a
combination of at least two of said elastomers.

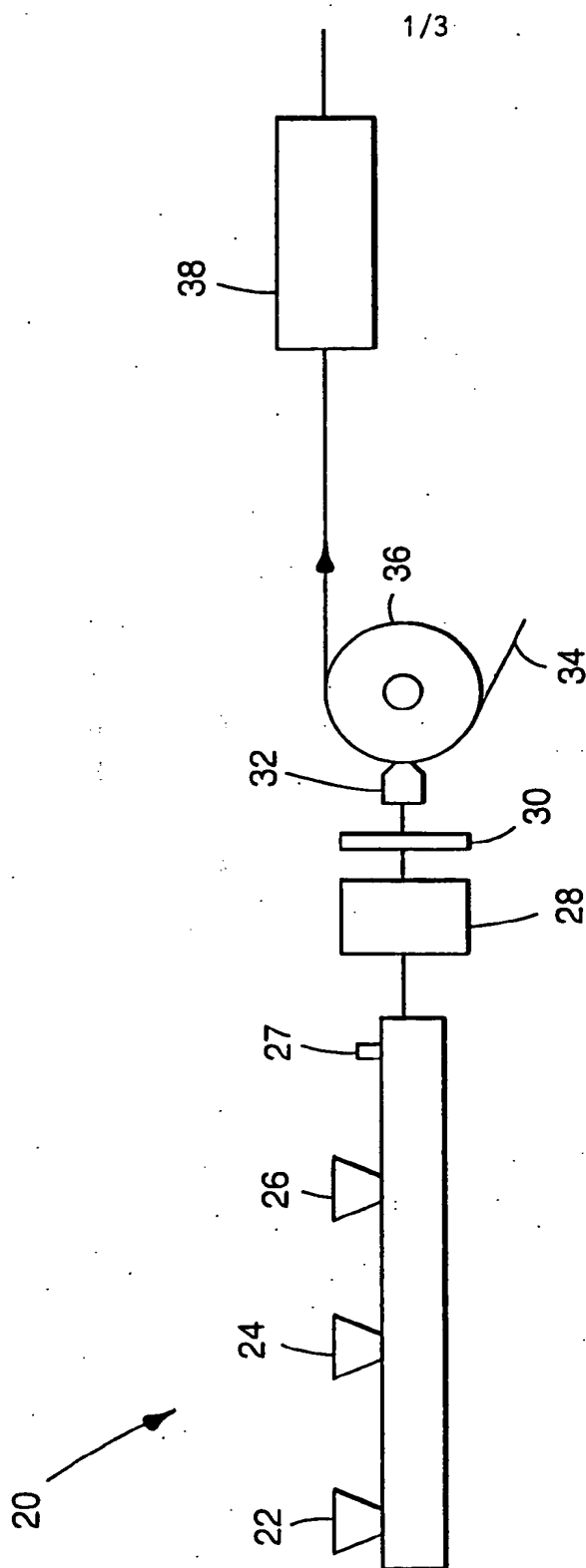


FIG.1

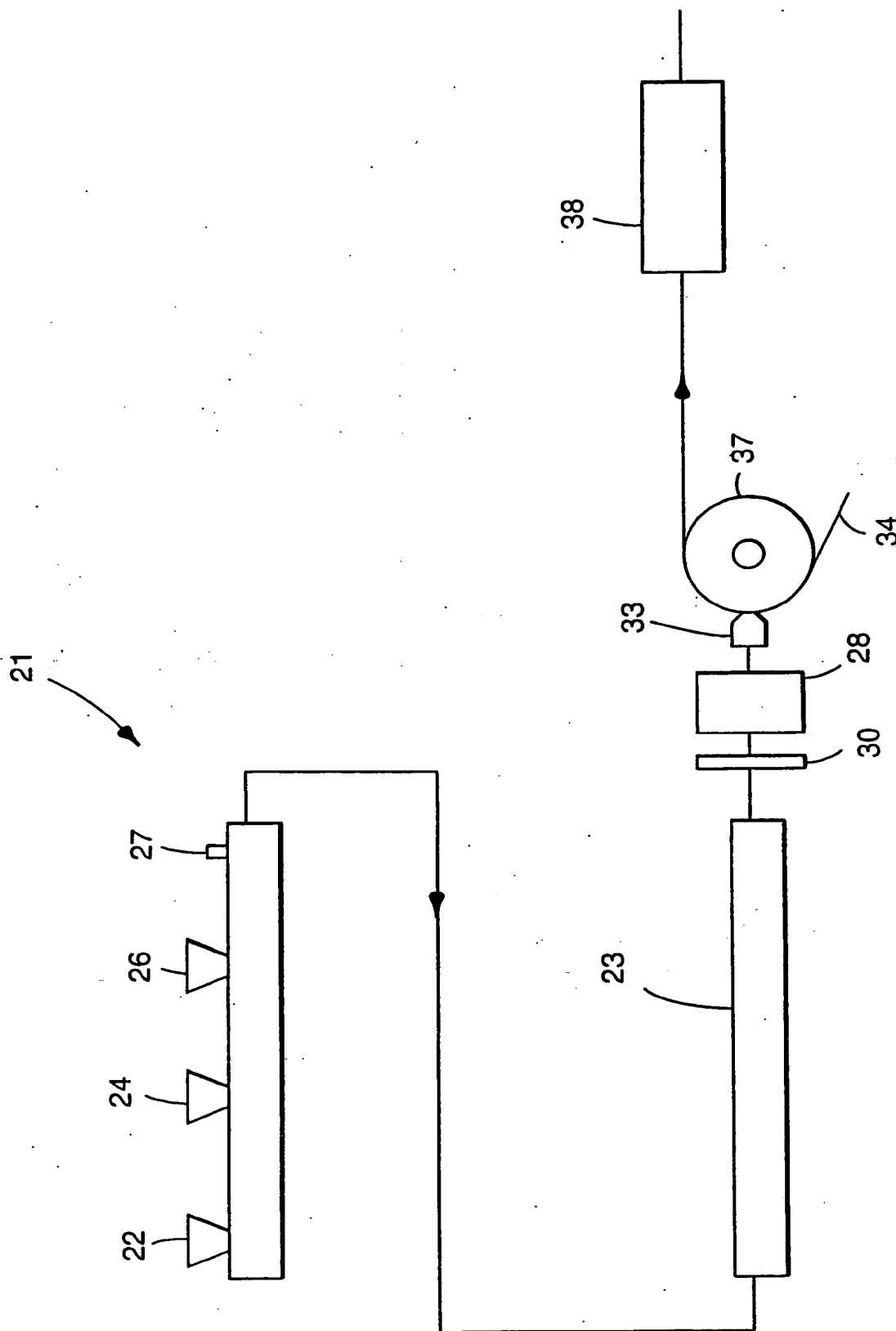


FIG. 2

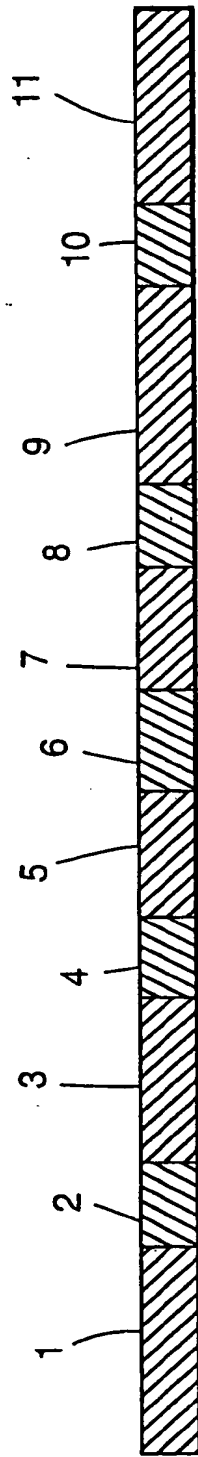


FIG. 4

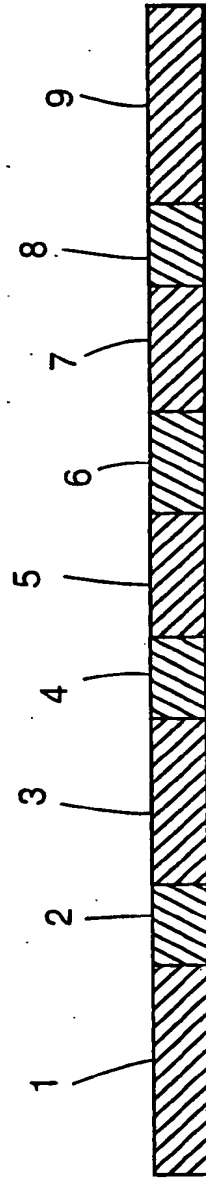


FIG. 3

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 93/09393

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 B29C47/10 B29C47/02 B29C47/40 B29C47/50 B29C47/64
B29C47/68 B29B7/48 C09J7/02 //B29K105:24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 B29C B29B C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,19 54 214 (PYTON AG) 6 May 1971 cited in the application	1,4-10
Y	see page 18, paragraph 1; claims 1-36; figures 1,2; example 1 cited in the application ---	2,3
X	DATABASE WPI Week 7906, Derwent Publications Ltd., London, GB; AN 79-11022B & JP,A,53 149 234 (MITSUI POLY CHEM KK) 26 December 1978	1
Y	see abstract; figure 1 ---	2,3
Y	EP,A,0 111 391 (POLYSAR LIMITED) 20 June 1984 see page 2, line 25 - page 6, line 10; claims 1-5; example 5 ---	2,3
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search

24 January 1994

Date of mailing of the international search report

21. 02. 94

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Authorized officer

Van Nieuwenhuize, O

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/09393

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 7, no. 213 (C-187)20 September 1983 & JP,A,58 113 280 (SONY KK) 6 July 1983 see abstract ----	5,9
A	DATABASE WPI Week 8338, Derwent Publications Ltd., London, GB; AN 83-767263 & JP,A,58 134 172 (TOPPAN PRINTING KK) 10 August 1983 see abstract ----	5,9
A	DE,A,41 11 739 (ERSTE CHEMNITZER MASCHINENFABRIK GMBH) 8 October 1992 see page 3, line 4 - line 62; claims 1,2; figure 1 ----	1,7
A	US,A,4 431 598 (R. KORPMAN) 14 February 1984 see column 2, line 52 - column 4, line 54 see column 5, line 15 - line 27; claims 1,2; figure 1 ----	1,4,6-8, 10
A	US,A,3 634 381 (W. LEHNERER ET AL) 11 January 1972 see claims 1-7; figure 1 ----	2
A	US,A,3 592 710 (W.J. YURGEN ET AL) 13 July 1971 see column 5, line 18 - line 31; claims 1,8,11-16; figure 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/09393

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		AU-B- 562793	18-06-87
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US-A-4431598	14-02-84	NONE	
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